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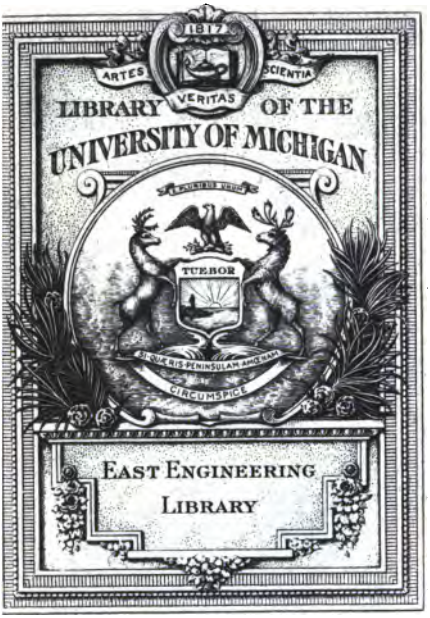
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CHEMICAL MONOGRAPHS

EDITED BY A. C. CUMMING, D.Sc.

No. II

The Chemistry of Dyeing

CHEMICAL MONOGRAPHS

EDITED BY A. C. CUMMING, D.Sc.

THE progress of Chemistry is so rapid that it is becoming a matter of ever-increasing difficulty to keep abreast of the modern developments of the science. The volume of periodical literature is so enormous that few can hope to read, far less assimilate, all that is published. The preparation of summaries has therefore become a necessity, and has led to the publication of various well-known journals devoted to the abstraction of original papers. For obvious reasons, however, these do not fully supply the wants of advanced students and research workers, and it is now generally recognised that monographs on special subjects are also needed.

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THE CHEMISTRY OF DYEING

BY

JOHN K. WOOD, D.Sc.

Lecturer in Chemistry, University College, Dundee

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TWENTY-FIVE PARK PLACE

1915

PREFACE

In writing this little book my principal aim has been to give a concise and connected account of the work which has been carried out, particularly during the last thirty years, with the object of throwing light on the nature of the dyeing process. As will appear from a perusal of the book itself, many of the common practices of dyeing and the phenomena connected with the process are found, on examination, to be in agreement with and easily explained by the general principles of Physical Chemistry, with which the reader is supposed to be familiar. The book may have, therefore, the effect of widening the student's outlook, by showing him that the principles which govern many of the operations of the laboratory apply with equal force to a large industry. Such information respecting the textile fibres and the dyestuffs as is necessary for a complete understanding of the principles of dyeing has been included in the book.

I hope that the work may also appeal to some of those actively engaged in the Dyeing Industry as well as to the student, and that it may have the effect of arousing in them a greater interest in the theoretical side of their work.

J. K. W.

Dundee, *January* 1913.

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The Chemistry of Dyeing

INTRODUCTION

By the term "Dyeing" we mean the colouring of various materials, especially textile fabrics, in such a manner that the colour is not readily removed by washing or rubbing the article; moreover, the colour must be distributed right through the whole material, and not lie simply on the surface as with a painted article.

The art of dyeing dates from prehistoric times and is of Eastern origin. Pliny gives a short account of the methods employed in Egypt in the first century, but in even earlier times dyeing operations were carried on in India, China, and Persia. From Egypt knowledge of the art travelled in a westward direction, but it was not until towards the end of the fifteenth century that the Dyers' Company was incorporated in London.

Previous to the middle of the last century, all the materials used as colouring agents were of natural origin, being chiefly obtained from various portions of trees and plants. Probably in the early stages of the development of dyeing, the colours produced were of a fugitive character and little better than stains,

but as time went on methods were discovered by means of which the colours could be made more permanent; the Egyptians, for example, were well acquainted with the use of alum for this purpose.

In 1856 the first artificial dyestuff was manufactured, and this marked the beginning of a new epoch in the dyeing industry. During the last fifty years thousands of other artificial colouring matters have been prepared, with the result that those of a natural origin have been almost completely displaced. The artificial dyes are, for the most part, more easily applied than the natural ones, as well as being more reliable; a much greater variety of colour is now possible than was the case prior to the introduction of the artificial colouring matters.

As regards the materials which are dyed, these consist principally of goods to be used for clothing, upholstery, etc., composed of products of an animal or vegetable origin. These animal and vegetable substances differ very much in their chemical characters and in their behaviour towards dyes and other chemicals. In addition to this, the dyes also show great diversity of constitution and properties. It will be at once apparent, therefore, that before studying the dyeing process and endeavouring to ascertain the nature of the union between material and dye, it is necessary to be familiar with the properties of the more important textile fibres and with the different groups of colouring matters.

SECTION I

The Chemical Composition and Properties of the Textile Fibres.

THE chief textile fibres with which the dyer comes into contact are cotton, linen, jute, wool, and silk. It is customary to divide these into two groups, the first three being classed as vegetable fibres and the remaining two as animal ones; as will be shown shortly, there are marked differences between the two kinds of fibres.

A microscopical examination of the fibres reveals the fact that they are structurally very different. The wool fibre has the most complex structure, being made up of cells of three distinct kinds; silk, on the other hand, might be said to be devoid of structure, the fibre, as it issues from the spinneret in the head of the worm, consisting simply of a long double cylinder. The vegetable fibres are composed of hollow cells, each cell having a central canal or *lumen* running through it. In the case of cotton the fibre consists of a single cell, whilst with linen and jute the cells are grouped together in bundles to form the fibres.

It is with the differences of a chemical nature shown by the fibres that we are, however, principally

concerned, for it is largely upon these that the difference in the behaviour towards dyestuffs depends.

Cotton and Linen.

Cotton and linen consist essentially of the polysaccharose cellulose, and exhibit in general the properties of that substance; instances of peculiar behaviour, such as that of the cotton fibre towards concentrated solutions of alkalis, are traceable to the structure of the fibre and have no connection with its chemical composition. Solutions of strong acids have a hydrolysing action on the fibres, which are converted ultimately into dextrin and glucose. Even with very dilute solutions of such acids gradual disintegration of the fibre is produced if the acid solution is allowed to dry upon the fibre. Weak acids such as acetic and formic acids have no appreciable action upon cotton and linen. As is well known, concentrated nitric acid either alone or in conjunction with sulphuric acid converts cellulose into various nitrates, often incorrectly called nitro-celluloses; this property is now made use of for preparing from cotton and other forms of cellulose certain kinds of the so-called artificial silks (see later). From the foregoing statements it will readily be concluded that great care must be taken when dyeing cotton and linen to avoid the use of dyebaths containing considerable amounts of strong acids, whilst even when the proportion of such acids is very small the treatment in the bath must be followed by thorough washing of the material in order to remove the small amount of acid present in the cloth, and so prevent the

destruction of the fibre which would result from the gradual concentration of the acid.

Dilute solutions of alkalis have no appreciable action on cotton or linen, but cold concentrated solutions of sodium or potassium hydroxide have a remarkable effect upon the former fibre. The cotton fibre is naturally flat and twisted spirally, but after treatment with the alkali it is found to be cylindrical and straight. The lumen practically vanishes during this treatment, whilst the fibre becomes translucent and has a superior attraction for colouring matters as compared with the natural fibre. This behaviour of cotton was noticed first by Mercer, and is now taken advantage of for the manufacture of the so-called mercerised cotton.

Solutions of hypochlorites, especially when warm, convert cotton and linen into a substance to which Witz has given the name of oxycellulose. This substance possesses distinct acid properties, and has a greater attraction for dyes of the basic class than have the natural fibres.

Jute.

Jute, although resembling cotton and linen in its behaviour towards acids, differs from those fibres in its chemical composition. Cross and Bevan,[12] who have made a study of the subject, have given the name of bastose to the substance of which jute is composed. An insight into the nature of this substance is afforded by the fact that on treatment with alkalis it yields cellulose, together with substances

related to the tannins. The researches of Cross and Bevan (*loc. cit.*) have shown that bastose, which is one of the ligno-celluloses, may be regarded as a complex made up of ordinary cellulose, a penta-cellulose containing an aldehyde group and yielding furfurol on hydrolysis, and a substance of the nature of a quinone, which, on chlorination and reduction, yields derivatives of the trihydric phenols. Owing to the presence of this latter constituent, jute behaves towards basic dyes in the same manner as cotton which has been mordanted with tannic acid.

Wool.

Wool and silk differ very materially in their chemical composition from the vegetable fibres. Wool is chemically, as well as structurally, the most complex of the common textile fibres; it contains nitrogen and sulphur in addition to carbon, hydrogen, and oxygen. The amount of sulphur is only small and varies in different samples. It appears probable that this amount of sulphur does not all enter into the composition of the fibre itself, but that the bulk of it is present as a loosely combined compound, since most of the sulphur can be removed from wool by the agency of alkalis without causing any apparent change in the structure of the fibre. The small amount of the element not so removed, and forming about 0·5 per cent. of the total weight of the fibre, probably enters into the composition of the wool-substance. The name of keratin has been given to the substance of which wool is composed. It is of

the nature of a protein, and like all such substances is amphoteric* in its reactions. Hydrolysis with solutions of alkalis breaks up the keratin into simpler substances. One such substance is lanuginic acid, which was isolated by Champion,[11] and afterwards more thoroughly examined by Knecht and Appleyard.[87] It is prepared by dissolving purified wool in a moderately concentrated solution of barium hydroxide, and then passing carbonic anhydride through the liquid to precipitate the barium; the precipitated barium carbonate is filtered off and the filtrate mixed with a solution of lead acetate. The precipitate obtained contains the lanuginic acid; it is washed, suspended in water, and the lead thrown down as sulphide by means of sulphuretted hydrogen. On evaporating the filtrate from the lead sulphide a dirty yellow residue remains, which is the lanuginic acid. Knecht and Appleyard (*loc. cit.*) found this substance to give the ordinary protein reactions; it contains sulphur and dissolves in water, forming a solution which is not coagulated by heat. Further

* An amphoteric compound is one which is so constituted that it is capable of acting either as an acid or a base. The simplest organic substance of this kind is glycine; by virtue of the carboxyl group which it contains, it is able to react with alkalis and form salts in which it takes the part of the acid, while the presence of the amino group makes it possible for glycine also to form salts by union with strong acids, and in the latter case the glycine is playing the part of a base. Some metallic hydroxides, such as, for example, those of aluminium, zinc, lead, etc., also possess the power of forming two classes of salts, in one of which they act as a base and in the other as an acid.

reference to this compound will be made when dealing with the theories of dyeing.

The presence of aromatic amino groups in keratin is indicated by the behaviour of wool towards nitrous acid, a diazo compound being formed which can be afterwards coupled with a phenol in the usual manner. The fact that wool, when treated with dilute solutions of sulphuric or hydrochloric acid, absorbs and holds tenaciously part of the acid, is further evidence of the possession of basic properties by the fibre.

As regards their effect upon the physical properties of the wool fibre, acids are nothing like so destructive as in the case of the vegetable fibres. Dilute, hot solutions of strong acids, even, have little effect upon the strength of the fibre, but concentrated solutions gradually destroy it. Nitric acid, as with many proteins, turns wool yellow owing to the formation of xanthoproteic acid.

On the other hand, alkalis are much more severe upon wool than upon cotton and linen. Dilute solutions of alkaline hydroxides, even in the cold, weaken the fibre, whilst on heating the wool gradually dissolves.

Silk.

Silk bears a considerable resemblance to wool in its chemical properties. It is also a protein, but, unlike wool, contains no sulphur. Raw silk consists of two substances, sericin and fibroin. The former constitutes about 25 per cent. of the whole; it is

sometimes called silk glue, and has the effect of making the fibre stiff and harsh in feeling. Before being manufactured into silk goods the raw fibre is scoured by means of a solution of soap; this has the effect of removing the sericin, leaving the ordinary well-known glossy fibre which consists of fibroin. Fibroin gives the usual reactions of proteins, and on hydrolysis is resolved into a mixture of amino acids; like keratin it contains the aromatic amino group.

Silk resembles wool in its behaviour towards acids and alkalis, but is rather less sensitive to the action of these substances. Concentrated solutions of mineral acids and hot solutions of alkaline hydroxides dissolve the fibre.

Artificial Silks.

In addition to the previously described substances, some account must be given of certain artificial products now in considerable use for textile purposes. Numerous attempts have been made to prepare artificial products which should have the properties of silk but be capable of being produced at a lower cost. Of these so-called artificial silks, three have proved commercially successful up to the present. The starting-point in the preparation of all these varieties of artificial silk is some form of cellulose (a variety of artificial silk has been prepared from gelatin, the threads being treated with formalin to render them insoluble, but this process has met with no appreciable success). About half the artificial

silk used at the present is prepared from the cellulose nitrates; solutions of these substances in alcohol, ether, and other solvents are squirted through capillary tubes into the air. A thread is in this way produced which is, however, of too inflammable a nature to be fit for use in the making of textiles; by denitration with various mixtures a product is ultimately obtained which does not exceed cotton in inflammability. A second process for the preparation of artificial silk, giving rise to the product known as **Glanzstoff**, consists in dissolving cellulose by means of an ammoniacal solution of copper oxide, and forcing the liquid through fine tubes into a solution of sulphuric acid or some other coagulating medium.

Viscose silk is another form of artificial fibre now being manufactured in considerable quantities. Cellulose is treated with a 15 per cent. solution of sodium hydroxide, and the resulting mass, after being squeezed, is then submitted in a closed vessel to the action of carbon bisulphide. After several hours a product is obtained which is known as viscose, from the fact that when dissolved in water it gives rise to an extremely viscous liquid. By squirting this product through platinum jets into solutions of ammonium salts threads are obtained which can be made up into textiles.

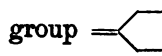
It will be evident from the description which has been given of the methods of preparation of artificial silk, that these products are chemically more allied to cotton than to silk. Saget and Süvern have stated that whereas natural silk contains about 17 per cent. of nitrogen, the various makes of artificial fibre all contain less than 0·25 per cent. of that element.

Consisting essentially of cellulose, the artificial silks behave towards reagents in the same way as cotton does. The artificial fibres also, for the most part, resemble cotton in their behaviour towards dyestuffs, the principal point of difference being that the silk from the cellulose nitrates can be dyed directly with dyes of the basic group.

SECTION II

Dyes and their Properties.

As was stated in the introduction, thousands of artificial colouring matters are now known. It is not within the scope of the present work to enter into a full consideration of the constitution and methods of preparation of the colouring matters; for information on these subjects the reader may be referred to Cain and Thorpe's work on *The Synthetic Dyestuffs*.

It has been found that these substances belong to certain classes of organic compounds, so that it is evident that the question of constitution enters into the problem as to whether a particular substance shall be a dyestuff or not. Witt came to the conclusion that every dyestuff must contain one or more of certain groups which determined the character of the dye, and which he called **chromophores**. Amongst such groups may be mentioned the azo group $-N=N-$, the para quinone group  , etc. The simplest substance containing a chromophore was called a **chromogen**. In the case of the azo group, azo-benzene would be the chromogen. Azo-

benzene, however, though highly coloured, is not a dyestuff, and cannot be used for the dyeing of textile fabrics. The presence of a second group, called an **auxochrome** group, is necessary before the chromogen can become a dyestuff. The auxochrome confers salt-forming properties on the compound, and is in general either the amino or the phenolic group. It will be seen, therefore, that all substances which act as dyestuffs must possess either basic or acidic properties.

From the point of view of the dyer it is much better to classify the colouring matters according to their methods of application to the textile fibres rather than according to their chemical constitution, although, of course, the method of application is dependent on the constitution. When the practical method of classification is adopted it is found that the dyes fall into six or seven different groups.

The Basic Dyes, as their name indicates, are basic compounds, and are employed in combination with hydrochloric acid or zinc chloride. Dyes of this class can be applied directly to wool and silk, but an acid mordant such as tannic acid or a fatty acid is necessary in order to fix them upon cotton or linen. Jute, owing to its different chemical composition, behaves towards dyes of this group differently from cotton, and can be dyed directly. Many derivatives of triphenyl-methane (such as Magenta, Methyl Violet, Malachite Green, etc.), and similar substances, amino-azo compounds, acridine derivatives and certain phthaleins, such as Rhodamine, belong to this group of colouring matters. It must be noted that the

introduction of the sulphonic group into any of the above types of compound destroys the basic character of the dye.

The Acid Dyes consist of the sodium salts of sulphonic acids of all kinds. Dyes of this group are of particular importance for the dyeing of the animal fibres, to which the colouring matters can be applied directly without the use of a mordant being necessary. The acid dyes are seldom used for the dyeing of the vegetable fibres; when employed for this purpose, a basic mordant such as alum is required. Nitrophenols also belong to this class of dyes.

The Direct Cotton Dyes form a very important group of colouring matters, since they possess the property of dyeing cotton and linen, as well as wool and silk, without requiring the aid of a mordant. They are salts, and are azo compounds derived from diamines such as benzidine, tolidine, etc.

A number of other colouring matters capable of direct application to cotton have come into extensive use of late years. These are the dyes known as **sulphur** or **sulphide** colours, and they are prepared by fusing certain aromatic amines, etc., with sulphur and sodium sulphide. The products obtained are insoluble in water and cannot be purified by recrystallisation, so that the actual composition of these dyes cannot be readily determined; probably the majority of these colouring matters consist of complex mixtures. Although insoluble in water, the dyes dissolve in a solution of sodium sulphide, and the solution to be used in the dyebath is prepared in this manner,

sodium sulphate and soda ash being added as assistants. It has been supposed that the solution contains the dye in the form of its leuco compound, the actual colouring matter being reformed on exposure to the air.

Mordant Dyes.—In distinction from the last group of colouring matters, we have a fourth class known as the **mordant** dyes, which are distinguished from other dyestuffs by the fact that the use of a mordant is invariably necessary in order to fix the dye, no matter what the nature of the material of which the fabric is composed. The mordants usually used are salts of aluminium, chromium, and iron. The majority of the natural dyestuffs belong to this class, and many valuable wool dyestuffs also belong to it. They are of an acidic character, and contain phenolic or carboxyl groups. The most important dye of this group is probably Alizarin, which is used very extensively for the dyeing of cotton as well as being employed in wool dyeing.

Vat Colours.—Another group of colouring matters form the class known as the **vat** colours. Up to a few years ago Indigo was practically the only member of this group, but during the last few years a number of other dyestuffs have been prepared, all of which are applied in the same way as the important colouring matter mentioned above.

The dyestuffs of this class are all capable of reduction, and it is the reduction product which is actually absorbed by the fabric. Some of the dyes of this group, as, for example, the Algole and Indanthrene colours, are only suitable for cotton, as they require

a strongly alkaline bath for their application. The solutions of the reduction products of dyes of this character are darker in colour than the original substance.

The Indigo, Thio-indigo, Helindone, and Ciba dyes, on the other hand, only require at the most a slightly alkaline bath, and can therefore be applied to the animal as well as to the vegetable fibres; the solutions of the reduced dyes are of a lighter colour than the original compounds. After the leuco compound has been absorbed by the fabric the original substance is reformed in the pores of the fibre by exposing the wet material to the oxidising influence of the atmosphere.

Developed Dyes.—The last group of colouring matters to be mentioned may be described as the **developed** dyes, since they are actually formed on the fibre by the interaction of the substances necessary for their preparation. The so-called mineral colouring matters, such as Chrome Yellow, belong to this group, the colour just alluded to being formed within the pores of the fibre as a result of the interaction of a lead compound with a solution of a bichromate.

Aniline Black, a well-known and very fast colouring matter for cotton, is also included in this class, as it is formed by oxidising an aniline salt with which the fabric has been impregnated. (In the more modern method the cotton is not first treated with the aniline salt, but is immersed directly in a bath containing the aniline salt and the oxidising agent; on heating the mixture the colouring matter is formed and deposited on the fibre.)

A number of azo dyes are also developed on the fibre; these are sometimes known as **ice colours** because of the fact that ice is frequently necessary to prevent the decomposition of the diazo compound, which is one of the reacting substances. The substance applied to the fabric may be a dyestuff itself or not; the only essential is that it must contain a primary aromatic amino group and so be capable of diazotisation. After the treatment with nitrous acid the colour is developed by treating the material with a solution of a phenol or an amine, when coupling takes place in the usual manner with the diazo compound.

Many of the direct cotton dyes which are not themselves very fast can be converted by diazotising and developing into very fast products. One of the most useful developers is β-naphthol. Of the amino compounds employed in this manner which are not themselves dyes, mention may be made of *p*-nitraniline, α-naphthylamine, benzidine, etc.; when these substances are made use of the phenol is usually applied to the cloth, which is then introduced into the cooled solution of the diazotised amine.

Application of the Dyes.

As regards the methods of application of the various types of dyestuffs to the different fibres, these have been sufficiently indicated in principle in the foregoing pages. Details as to the mode of working in the case of individual dyes are best obtained from the pattern books and notices issued by all the

leading manufacturers of dyestuffs. The principles underlying certain of the practices commonly followed may, however, be discussed here.

It is a common practice to add to the dyebath a substance known as an **assistant**. Two of the most commonly used assistants are sulphuric acid and sodium sulphate, while in the dyeing of silk boiled-off liquor or soap is frequently added to the bath. Sulphuric acid is used in conjunction with the acid dyestuffs. It acts upon the dyestuff which, as has been stated, is a salt of a sulphonic acid, and liberates the free colour acid which is the substance probably taken up by the fibre. The added acid (this is not necessarily sulphuric; acetic and formic acids are employed to a considerable extent in this connection) also has the effect of diminishing the solubility of the colour acid. This is because of the fact that the two substances give rise to a common ion, hydrion, and the law of mass action applies to this as to all such cases.

The question of the amount of acid to be added depends on the character of the dye. The more rapidly a colouring matter is absorbed by a fibre, the greater is the danger of the dyed material being uneven in colour. With a dyestuff, therefore, which is readily absorbed by wool, an excess of acid is to be avoided, so as to prevent the solubility of the colour-acid from being sensibly diminished; too rapid absorption of the dye will in this way be obviated. The same end can be attained by an addition of sodium sulphate in conjunction with the sulphuric acid; the sodium hydrogen sulphate formed

from the two substances is a weaker acid than the sulphuric acid itself, and has therefore less action upon the dyestuff, as it cannot compete so strongly for the base of the dyestuff, which means that a smaller amount of colour acid will be liberated. Owing also to sodium hydrogen sulphate being a weaker acid than sulphuric acid, an excess of the former has much less effect on the solubility of the colour acid than is produced by an excess of sulphuric acid. A too rapid deposition of colouring matter is also avoided by working at a low temperature.

When acid dyes are employed for dyeing silk an acid is again added to the bath for the same reasons as have been mentioned in the case of wool, and the same considerations are necessary in determining the quantity of acid to be added. When it is necessary to regulate the rate at which the dyestuff is absorbed, an addition of soap or of boiled-off liquor may be made instead of sodium sulphate.

As regards the other classes of dyestuffs, the members of the direct cotton group are the ones for which the use of an assistant is most necessary. The dyes of this group, it has been already stated, have the character of salts, and it is customary to add along with them to the dyebath some other salt, such as sodium sulphate or chloride. The effect of this addition is exactly similar to that caused by the addition of an excess of acid to the acid dyes, that is, by increasing the active mass of one of the ions to which the dyestuff gives rise, the solubility of the dye is diminished. Too rapid deposition of the dye upon the fibre is in this case prevented by

adding a substance of an alkaline character, such as soda ash, along with the sodium sulphate, the alkali tending to keep the colouring matter in solution. When silk goods are being dyed, the sodium sulphate is replaced by boiled-off liquor or soap.

No addition is made to the bath with the basic dyes unless it is desired to retard the rate of absorption, in which case a small amount of sulphuric or other acid is added; this has a solvent action on the dye and brings about the desired effect.

The Condition of Dyes in Solution.

Of late years a considerable amount of work has been done in connection with the mode of existence of dyestuffs in aqueous solution, and as the subject is of interest because of its bearing on the principles underlying the dyeing process, an account of the more important work in this direction will now be given.

As has been indicated in the earlier part of the section, the dyes of the acidic, basic, and direct cotton groups are all of the nature of salts, and assuming, therefore, that they form true solutions when added to water, they should be largely ionised, diffuse through a parchment membrane and, in fact, exhibit all the phenomena of salts in general; probably in some cases where the acid or the base, or both of these, is weak, a certain amount of hydrolysis would take place. It will be evident that a great deal depends on whether the dyes exist in a state of true solution or not, and most of the recent work has been directed to the settlement of this problem.

Amongst the earliest observations dealing with this subject may be mentioned those of Pfeffer,[47] who noticed that some of the basic colouring matters, such as Methylene Blue and Methyl Violet, are able to pass through the wall of a living cell and colour the protoplasm. Obviously, therefore, dyes such as those mentioned must exist in true solution, for unless such were the case no dialysis could take place. Later investigations go to show that this property of existing in a state of true solution is not one which applies to dyes in general.

True and Colloidal Solutions.—By means of dialysis experiments and also as a result of examining solutions with the ultra-microscope, Freundlich and Neumann[22] have come to the conclusion that dye-stuffs should be divided into three classes, and a similar conclusion was arrived at by Biltz and Pfenning.[6]

The first group consists of those colouring matters which diffuse readily through parchment paper, and which are therefore present in true solution; amongst the dyes of this class may be mentioned Chrysoidine, Bismarck Brown, Auramine, Eosine, Methylene Blue, Safranine, Picric Acid, etc.

The second group contains dyes which form solutions of a semi-colloidal nature, that is to say, dialysis takes place, but at a very slow rate. Magenta, Methyl Violet, Capri Blue, and Nile Blue are a few of the dyes which fall into this group.

The third class contains the dyes which form colloidal solutions proper, as indicated by their non-diffusibility through a membrane, and by the fact

that the solutions, when examined with the ultra-microscope, are not optically void. Many of the dyes of the direct cotton group, such as Congo Red, Benzopurpurin, Benzoazurin, etc., are of this type, but the property of forming colloidal solutions is not confined to the direct cotton colours; Night Blue, Induline, Alkali Blue, etc., all form solutions of this nature.

Freundlich and Neumann (*loc. cit.*) divide the dyes of the third group into two sections, according to whether they have a marked influence or not on the properties of the solvent. The first section contains the dyes which form solutions of the same nature as that given by arsenious sulphide. They are called "suspensoids," and are precipitated by the addition of small quantities of salts. As regards the dyes of the other section, called "emulsion colloids," they require the addition of considerable amounts of salts before precipitation takes place, and influence very considerably the surface tension and other physical properties of the solvent; the solutions formed by dyes of the latter type bear a resemblance to solutions of gelatine. Night Blue is a colloid of the latter kind, while Congo Red is one of the colouring matters included in the first sub-section.

Molecular Complexity of Dyestuffs.—Biltz and Pfenning (*loc. cit.*) have drawn the conclusion that the dialysing power of a dyestuff depends on its molecular complexity. If the molecule of the dye contains less than forty-five atoms the substance will diffuse rapidly through parchment or through a collodion membrane, but as the number of atoms in

the molecule increases, the rate of diffusion diminishes; with dyes containing between fifty-five and seventy atoms in the molecule the velocity of dialysis is very small, while when the number of atoms exceeds seventy dialysis ceases altogether.

This relationship between the complexity of the substance and the rate of dialysis is, however, influenced to a certain extent by the composition and constitution of the substance. It was found, for example, that the introduction of the sulphonic acid group into a compound has a marked effect in increasing the dialysing capacity of the substance; dyes of the Malachite Green series containing two or three sulphonic acid groups pass readily through a membrane even when the number of atoms in the molecule exceeds seventy. Dyes having a constitution allied to that of Alizarin, on the other hand, dialyse less readily than would be expected from the number of atoms contained in the molecule.

Pelet-Jolivet and Wild[45] agreed with the previously mentioned investigators in coming to the conclusion that dyes can be divided into three classes according to the character of the solutions they form, but did not always agree as to the class in which certain dyes should be placed. Their methods of investigation included determinations of electrical conductivity and the use of the ultra-microscope. They also determined the effect of dye solutions upon diazo acetic ester and noticed no catalytic action, from which they naturally concluded that the colouring matters examined did not undergo hydrolysis in aqueous solution. This is opposed to the views commonly

held, and it would be of interest to ascertain whether the results can be confirmed. Biltz and Pfenning[7] have made determinations of the electrical conductivity and osmotic pressure of solutions of dyestuffs which had been freed from admixed inorganic salts by the process of dialysis. The conductivity results seem to show that the substances examined behave as normal electrolytes, although they do not obey Ostwald's rule regarding the dependence of the molecular conductivity on the basicity of the acid. The results of the determinations of osmotic pressure showed that a dye solution has in many cases a complex character, as products of association, ionisation, and hydrolysis may be existing together in a state of equilibrium. With solutions of monosulphonates the association and hydrolysis products are the most important, and the molecular weight calculated from the osmotic pressure is much higher than the theoretical value. With the disulphonic derivatives ionisation practically balances association, so that the molecular weights which are determined agree on the whole with the theoretical values. When the number of sulphonic acid groups exceeds two, the question of ionisation becomes of most importance, and owing to the extent to which this takes place the observed values for the molecular weights are considerably smaller than the theoretical values.

Determinations of the electrical conductivity of solutions of dyestuffs have also been made by Knecht and Batey,[38] some of the dyes experimented with, as for example, Benzopurpurin, being amongst those

classed as colloids by other investigators. They found the solutions to be good conductors, and the results obtained with dilute solutions were such as to indicate a high degree of ionisation. The results of the conductivity experiments were supported by the values obtained for the molecular weights of the dyes by the boiling-point method. With Benzopurpurin, Soluble Blue, and Chrysophenine, the observed elevation of boiling-point of the aqueous solution was such as to indicate a considerable amount of ionisation. The authors mentioned also found Benzopurpurin to have a high rate of dialysis, and they are consequently opposed to the view that it and many other dyestuffs, especially those of high molecular weight, exist in the state of colloidal solution.

Results of an interesting and important character have been obtained from the investigation of solutions of Congo Red and allied colouring matters. Bayliss[3] showed that although this colouring matter will not pass through a parchment membrane and also exhibits other properties associated with colloids, yet it exerts an osmotic pressure equal to that which would be expected if it was present in a state of true solution in the unassociated form. This result was only obtained, however, when the outside vessel was filled with distilled water; if solutions of acids, bases, or salts were used instead of water, the values of the osmotic pressure determined were of considerably lower magnitude. Bayliss considered the electrolyte to have the effect of causing the molecules of dye to collect together to form aggregated particles.

Similar experiments were carried out by Biltz and Vegesack,[8] making use of Congo Red, Benzopurpurin, and Night Blue. The results obtained with Congo Red, previously freed from admixed salts by prolonged dialysis, confirmed those obtained by Bayliss. With water in the outer vessel the value calculated for the molecular weight was 602, the theoretical value being 696, whilst the result obtained when the outer vessel was filled with a salt solution of the same conductivity as the dye solution was 2333. From a consideration of the equilibrium between the ions of Congo Red and those of sodium sulphate, the conclusion was drawn that if the solute is not polymerised the apparent molecular weight of Congo Red should be three times the normal value, that is, 2088; as this figure is only slightly different from the one actually determined, Biltz and Vegesack came to the conclusion that Congo Red only undergoes slight polymerisation in solution. Results of a similar character were obtained with Night Blue, but in this case complications were introduced because of the fact that a certain amount of hydrolysis takes place.

The investigation was extended to the examination of commercial preparations of certain dyestuffs. Many of these products contain a certain quantity of salts, chiefly sodium sulphate; in Congo Red the amount of impurity is about 26 per cent. The molecular weight of Congo Red, as determined from this sample, was found to be about 7380, from which the conclusion was drawn that association takes place in the presence of salts.

This view of the effect of electrolytes on the molecular complexity of dyes such as Congo Red, Night Blue, and Benzopurpurin, received additional support from ultra-microscopic examinations of the solutions. The effect of the electrolyte appears to become more pronounced when the solution is kept, and the polymerisation is greater in concentrated than in dilute solutions. The temperature of the solution also appears to have a marked influence on the degree of association; Biltz and Vegesack, from the determination of the osmotic pressure at different temperatures, came to the conclusion that in a solution of Night Blue the degree of association at 0° was 6·7, at 25° it was 3·05, while at 70° the value was only 1·9.

Anomalous Behaviour of Dyestuffs on Dialysis.—An important paper dealing with this subject was published recently by Donnan and Harris.[15] Several of the observations they made confirmed those of the previous workers on this subject, as, for example, that Congo Red gives an osmotic pressure when measured against distilled water which agrees approximately with the value which would be obtained for a true solution in which the dye was present as single molecules. From the determinations of electrical conductivity they drew the conclusion that the dye exists to a very considerable extent in the ionised condition.

Amongst the most important of their observations were those dealing with the dialysis of solutions of dyes of the Congo type. It was found that both with Congo Red and Benzopurpurin 4B a peculiar

"membrane hydrolysis" takes place, sodium ions in company with hydroxyl ions diffusing out of the dialyser, while the free dye acid, an acid salt, or some other insoluble phase remains behind. It was found possible to prevent this hydrolysis by adding to the dye solution an alkaline hydroxide, the quantity of alkali required depending on the temperature and concentration of the solution of colouring matter. It is evident, therefore, in the light of these observations, that the osmotic pressure observed with a solution of a colouring matter like Congo Red does not correspond with the ordinary state of osmotic equilibrium.

Donnan and Harris also confirmed the fact that the osmotic pressure of Congo Red is lowered in the presence of certain electrolytes, but they threw a considerable amount of new light on this matter, and were led to conclusions which must, if they are accepted, and the author sees no reason for adopting any other attitude, lead to the abandonment of some of the views previously held.

It was found that when Congo Red and sodium chloride were introduced into a dialyser, the sodium chloride distributed itself unequally on the two sides of the parchment membrane, and a reversible ionic equilibrium was ultimately established, the concentration of sodium chloride at equilibrium being higher on the side opposite to that occupied by the dyestuff. It was found that this membrane equilibrium is necessary from thermodynamical considerations, and that it is one of a group of phenomena of a general character. It is obvious that because of the unequal distribution of the salt on the two sides of the

membrane an opposed osmotic pressure will be set up, and this is probably the cause of the smaller values obtained with solutions of dyes containing dissolved salts, or where the outer vessel contains salts.

All the conclusions which have been drawn, therefore, regarding the molecular complexity of dyes in solution from measurements of the osmotic pressure are valueless when another electrolyte is present, unless account be taken of the unequal distribution of the foreign electrolyte. The subject is one of great interest, and no doubt further experiments will be made in the near future which will shed additional light on the condition of dyestuffs in solution.

While at present, in view of the results obtained by Donnan and Harris, it would be unwise to lay too much stress upon the results of dialysis experiments with solutions of dyes, it is yet quite clear from the evidence gained by the use of the ultra-microscope that many colouring matters in aqueous solution exist to a greater or lesser extent in the colloidal condition. On the other hand, the aqueous solutions of other dyes are optically void, and appear, from determinations of the electrical conductivity, to be ionised to a considerable extent; in such cases we are justified in believing that the dye is present in a state of true solution.

SECTION III

The Nature of the Dyeing Process.

IT is not surprising that in the case of an industry so old and so universal as is that of Dyeing many speculations should have been made as to the nature of the process by which the colouring matter becomes fixed on the fibre in an insoluble form. An attempt will be made in the following pages to give some account of the different ideas which have from time to time been held on the subject, together with the experimental evidence on which these theories have been based, and the criticisms which have been brought against them. As can readily be imagined when one considers the diversity of substances involved, both the dyes and the fibres, the subject is one fraught with great difficulty, and even yet different views are held by chemists as to the mechanism of dyeing.

Although unanimity of opinion has not yet been arrived at, there are certain ideas, which will be discussed at a later stage, which may be brought into harmony with all the different opinions, and so it is not impossible, unlikely as such a thing may at first sight appear, to arrive at a theory which shall apply to all cases of dyeing.

The Mechanical Theory.

The earliest idea respecting the dyeing process was that it was of a purely *mechanical* character. Explanations of the process on these lines were given about the middle of the eighteenth century by Hellot, Le Pileur d'Apligny, and others. Hellot stated that the heat of the dyebath causes the pores of the fibre to open so that the particles of colouring matter can enter and be deposited; when the fibre is removed from the dyebath the pores contract, and so the dye is retained in position. As regards the various substances used in preparing the material for dyeing, these were also considered to be retained in the pores of the fibre, and were thought to coat the particles of dye with a kind of varnish.

The difference in the behaviour of different fibres towards the same dyestuff was a phenomenon with which the early dyers were thoroughly familiar, and this was also explained on a purely mechanical basis, Le Pileur d'Apligny suggesting that it was to be attributed to the difference in size of the pores of the various fibres, so that in some cases the particles of dye were too large to enter the pores, or, if they entered, the contraction on cooling was insufficient to permit of the dye being retained.

Although the majority of chemists at the present day are of the opinion that the dyeing of a piece of wool or cotton is not to be accounted for in such a simple manner as the above ideas would suggest, yet there are some who still adhere to the mechanical theory of dyeing, and there are certain cases where

the fibre certainly does appear to act in a mechanical manner. Amongst the later supporters of this theory may be mentioned Hwass,[33] von Perger,[46] and Spohn.[55]

Stress is laid on the fact that no definite compound of a fibre and a dyestuff has ever been actually shown to be produced during the dyeing process, and also on the retainment of many of its original properties by a colouring matter after it has been fixed upon the fibre. The rubbing off of the colour which is frequently observed with dyed goods, and the possibility in some cases of separating the dye from the fibre by the process of sublimation, are also considered to favour the mechanical conception of the character of the dyeing process.

A property common to all dyestuffs is, that if a fibre is introduced into a very dilute solution of the colouring matter practically the whole of it is taken up and is firmly retained, even when the dye is one for which the fibre in question may naturally have little affinity. This phenomenon is attributed to the forces of capillarity and adhesion, and it is argued by the supporters of the theory that similar forces must come into play and be responsible for all the results which follow the introduction of a fibre into a more concentrated solution of a colouring matter, such as is actually employed for the dyeing of a fabric.

While it is probable that the forces of adhesion and capillary attraction do come into play to a considerable extent, it is scarcely justifiable to conclude that all the phenomena of dyeing can be explained as resulting from the operation of those forces.

Reference may also be made to the views of Rosenstiehl,[50] who pointed out that solids, under the influence of pressure, can be made to adhere rigidly to one another. He considered the fixation of dyes to be brought about in this manner, the pressure necessary to make the dye adhere to the fibre being the osmotic pressure of the solution, this osmotic pressure being increased by the addition to the dyebath of the assistants, such as acids and salts, commonly added to the bath.

The experiments of Dreaper and Wilson[17] go to show that to regard the dyeing process as a purely mechanical one is to take up an untenable position. It was shown that when Night Blue is absorbed by silk at a temperature of 15° the whole of the colouring matter can be subsequently removed from the fabric by means of alcohol or by treatment with a boiling solution of soap; if, however, dyeing takes place at a temperature of 40° and upwards a portion of the dye appears to be taken up in a different manner, and cannot be removed by means of the above-mentioned agents. In all these experiments the total quantity of the dye upon the fibre was maintained constant, so that the results must really be due to a difference in the mode of existence of the colouring matter when fixed under the different conditions of temperature. Similar results were obtained in the case of a number of other colouring matters. In these cases, therefore, it appears obvious that something in addition to mere mechanical action is necessary to explain the fixation of the dye.

There is one sense, however, in which the

mechanical theory may be accepted, and that is in connection with the fixation of mordant colours, the so-called mineral colouring matters and the ingrain colours (that is, the azo dyes produced on the fibre). Spohn (*loc. cit.*) examined with the aid of the microscope cotton which had been dyed with lead chromate, and noticed the crystals of the colouring matter adhering to the colourless fibre. In such a case the colour is simply deposited in the pores of the fibre as it is formed by the interaction of the two reacting substances, and under such conditions the part played by the fibre is the purely mechanical one of a pigment carrier.

This view of adjective or mordant dyeing was supported by Weber,[59] who pointed out the difference in behaviour shown by Night Blue when applied to cotton in the absence of a mordant and in the presence of tannic acid. Under the former conditions the colouring matter retained its original properties and at once reacted with Naphthol Yellow, but when fixed in the presence of tannic acid no reaction ensued on subsequently treating the dyed cotton with the yellow dye.

The Chemical Theory.

Some little time after the period of Hellot, etc., Bergmann advanced the view that the process of dyeing is to be regarded as being of a purely *chemical* character, an interaction taking place between the fibre and the dye. Berthollet and others supported this view, which has persisted to the present day.

There is much to be said in favour of such an explanation of the dyeing process. With regard to the dyestuffs themselves, it has already been pointed out that the presence of groups of an acid or basic character is necessary before a substance can behave as a dye.

When we turn to the fibres, we find that the animal fibres possess an amphoteric character by virtue of which it would be possible for them to unite either with a base or an acid with the formation of a salt. This is in fact the way in which the advocates of the chemical theory of dyeing explain the substantive dyeing of wool and silk with the basic and acid dyes.

As regards cotton, the fact that it is practically devoid of acid or basic properties makes it an impossibility for any salt to be formed by the interaction of fibre and dyestuff, and the comparative inertness of cotton towards colouring matters is thus accounted for.

When we consider jute, we find that the fibre can be dyed directly with the dyes of the basic class, whereas such dyes can only be fixed upon cotton after the fibre has been mordanted with tannic acid or some other acid mordant. The difference in composition of cotton and jute makes it possible to easily explain this difference, for as has been already stated, jute is composed of ligno-cellulose, which is not unlike, in properties, cellulose which has been mordanted with tannic acid. Here again, therefore, the difference in behaviour towards colouring matters can be easily explained by taking into account the chemical nature

of the fibre. Certain of the objections against the theory have been mentioned in dealing with the mechanical theory.

A large amount of experimental work has been carried on during the last twenty-five years in support of the ideas embodied in the foregoing general statement. Knecht[34] showed that when wool was boiled with a moderately concentrated solution of sulphuric acid it gradually dissolved and gave rise to a light brown solution; if solutions of dyestuffs were added to the acid solution richly coloured precipitates were formed. By the careful neutralisation of the acid solution a substance was precipitated which, on drying, yielded an amorphous brown powder which was only sparingly soluble in acids, but dissolved readily in solutions of alkalis; when the alkaline solution was mixed with solutions of colouring matters and an acid then added, precipitates were formed similar to those which were obtained from the original acid solution. From these results Knecht drew the conclusion that the principal reason why sulphuric acid is added to the dyebath in the dyeing of wool is to act upon the fibre so as to produce a compound having properties similar to those possessed by the substance isolated; the compound so formed would then combine with the dye to form an insoluble product.

Reference has been made in an earlier chapter to the experiments made by Knecht and Appleyard[37] with lanuginic acid which they prepared from wool. When solutions of basic colouring matters were added to a solution of lanuginic acid, precipitates

were at once produced, and it was considered that this kind of change probably took place during the dyeing of wool with dyes of the basic class, a certain quantity of the fibre first undergoing decomposition with the formation of lanuginic acid, which would then react with the colouring matter.

Amongst other results obtained by Knecht and Appleyard (*loc. cit.*), some of a quantitative character may be referred to. When wool was dyed with certain acid dyes, it was found that if the quantity of one colouring matter, Picric Acid, absorbed by a given quantity of wool, was taken as the unit, then the amounts of two other dyes, Naphthol Yellow S and Tartrazine, absorbed by the same weight of wool, corresponded to one and to three-quarters of a molecule respectively; and the obtaining of these quantitative results was thought to be a strong piece of evidence in support of the chemical theory. Further quantitative results were given by Knecht[36] in a later paper.

Gelmo and Suida[24 56] also came to the conclusion that in the substantive dyeing of the animal fibres it is necessary for the fibre to first undergo a more or less profound hydrolysis, as a result of which products are formed which contain active salt-forming groups. This hydrolysis is greater in the case of wool than with silk, and is promoted by the presence of acid, and is necessary, according to the authors in question, for the satisfactory dyeing of the fibres. As regards the fixation of the dye, Gelmo and Suida considered that basic dyes are fixed by salt formation with the acid groups of the fibre substance, and acid

dyes by means of guanidyl or imidazole groups of the fibre.

It will be noticed from the preceding statements that by some supporters of the chemical theory, at any rate, the salt formation which is supposed to take place is not one involving particular groups of the fibre itself, but groups present in some product formed by the hydrolysis of the fibre. If this is really the nature of the action, then, according to Witt,[60] the dyeing of wool and silk with the acid and basic colouring matters should not be regarded as examples of substantive dyeing, but as instances of adjective dyeing, the products of the hydrolysis of the fibre acting as the mordant.

Other chemists, however, appear to regard the action as one in which the salt-forming groups of the fibres themselves are involved, and if such were the nature of the process then the operation would undoubtedly be one of substantive dyeing. Amongst those who may be said to have favoured this view was Weber,[59] who carried out some experiments of an interesting character. He argued that if the process of the substantive dyeing of wool and silk is one in which the fibre may be regarded as playing the part of an amphoteric compound, then even although an acid dye has been fixed upon the fibre it should still be possible to fix a basic one upon the same material, seeing that the acid group in the wool by means of which the basic dye is fixed would still be free. This was actually found to be possible in practice, a skein of wool being dyed with a large excess of Scarlet R, and then, after thorough washing, intro-

duced along with a white skein of equal weight into a solution of Magenta. It was found that the same weight of Magenta was absorbed by both skeins, thus showing the acid colouring matter to have no influence on the quantity of basic dye taken up. Of course it might be argued against this experiment that union had taken place between the two dyestuffs, but any such objection was confuted by the behaviour of the dyed material when treated with alcohol. The substances formed by the union of acid and basic dyes are readily soluble in that liquid, but it was found that only a small amount of the Magenta and none of the Scarlet was removed from the material by the solvent.

A number of experiments were carried out by Vignon,[57] which appeared to support the chemical theory of dyeing. Cotton, it is well known, has practically no affinity for the acid dyes, and this is attributed to the absence of groups of a basic character in the fibre. Vignon showed, however, that when cotton is heated in sealed tubes with an aqueous solution of ammonia or with the compound of ammonia with calcium chloride, its properties undergo considerable modification. After the material has been thoroughly washed with water and acids it is found to contain nitrogen, the amount of which may reach 3 per cent., and when a piece of the modified cotton is placed in a solution of an acid dye in company with a piece of untreated cotton, a considerable amount of the colouring matter is taken up by the modified fibre, while the ordinary cotton is scarcely stained. On the other hand, oxy-

cellulose, which has acid properties, has a greater attraction than ordinary cotton for basic dyes.

Vignon also measured the amount of heat which is generated when different fibres are immersed in solutions of acids and alkalis. The heat effect produced by cotton under such conditions is very small when compared with the effect produced with wool or silk, and this was considered as pointing to a certain amount of chemical action taking place with the animal fibres, as against practically no action with the cotton. This conclusion was strengthened by the observation that when the ammoniated cotton already referred to was immersed in sulphuric acid a considerable amount of heat was generated.

Physico-Chemical Objections to the Chemical Theory.—With the rise and development of physical chemistry, some of the arguments formerly brought forward in favour of this explanation of the dyeing process have been shown to have little bearing on the subject. It was, for example, noticed by Knecht[35] that when wool is dyed by means of a basic dye such as Magenta, the whole of the hydrochloric acid originally present in the colouring matter remains in the dyebath, the colour base alone being taken up by the fibre.

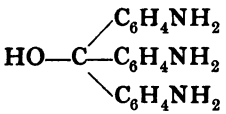
At first sight this appears to be conclusive evidence in favour of the chemical theory, but it was found by von Georgievics[25] that if the operation is carried out at a temperature below the boiling-point of water, the whole of the halogen of the dyestuff is not present in the bath at the conclusion of the dyeing process, but a portion is taken up by the fibre. Moreover,

if glass beads or pieces of unglazed earthenware are introduced into a solution of Magenta at the ordinary temperature, a certain quantity of colour is acquired by such articles, and the chlorine, at the end of the process, is present quantitatively in the bath; in cases such as these there is no possibility of chemical action taking place between the dyed object and the colouring matter, and some other explanation of the result must be sought for in place of that given by Knecht.

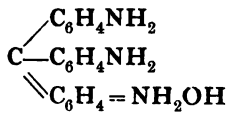
Such an explanation was suggested by Zacharias,[61] who pointed out that the dyes have the character of salts, and may therefore be more or less hydrolysed in aqueous solution into free colour base and free acid. As in all such cases, there will be a certain degree of hydrolysis depending on the concentration of the solution and on the temperature. As long as nothing happens to disturb the equilibrium, no further change will take place. The introduction of a piece of wool into the solution has, however, a disturbing effect, since it leads to the removal of one of the products of hydrolysis, the colour base, and in accordance with the laws of chemical equilibrium a further amount of the salt must be hydrolysed to restore the condition of equilibrium in the solution; it is at once evident that this process, if continued, will lead eventually to the complete decomposition of the dyestuff. The effect of temperature noticed by von Georgievics can also be explained quite easily on the same basis, for in the majority of cases the degree of hydrolysis of a salt increases with the temperature, so that at temperatures below the boiling-

point the process of hydrolysis might not be complete, the products of hydrolysis being a basic salt and some free acid; the basic salt would be absorbed by the fibre, which would therefore contain a certain amount of halogen.

Coloured and Colourless Modifications of Dye-bases.—Emphasis was also laid by the advocates of the chemical theory on the fact that when wool is introduced into water in which the colourless base of Magenta is suspended, the fibre acquires the magenta colour characteristic of solutions of the salts. It was pointed out by von Georgievics (*loc. cit.*) that it did not necessarily follow from this experiment that salt formation had taken place between the fibre and the colour base; the coloration of the fibre might be due simply to a change in the constitution of the colour base. The ordinary colour base has the carbinol form and is colourless, but von Georgievics obtained a second variety in which the substance has a quinonoid structure, and this modification has a magenta colour, and is probably the base to which the dye salts really correspond. The existence of this second form of the base was also indicated by electrical conductivity measurements made by Hantzsch and Osswald,[31] who were of the opinion that the bases of other dyes of the triphenylmethane series existed also in two different modifications.



Colourless form (para-rosaniline).



Coloured form (para-rosaniline).

In view of the existence of this second modification of the colour base, it is obvious that the production of colour when a colourless form of a base is taken up by a fibre does not necessarily indicate the formation of a salt.

Other Objections to the Chemical Theory.—One of the difficulties in the way of the chemical theory is that of explaining the behaviour of fibres towards the colouring matters of the direct cotton group. Both cotton and the animal fibres are dyed directly by these colouring matters, a fact which cannot be explained by any theory which involves the chemical nature of the fibre.

The recent experiments of Dreaper and Wilson,[18] who showed that acid dyes can be applied to silk from an alkaline bath, are also scarcely favourable to the chemical theory of dyeing.

The behaviour of dyed articles towards certain solvents was also considered by Witt[60] to be difficult to explain by means of the chemical theory. Silk, for example, which has been dyed with Magenta requires to be treated with a moderately concentrated soap solution before it gives up any of the colouring matter which has been fixed upon it, and one might therefore argue that the Magenta and the silk form a compound of considerable stability. When, however, the dyed silk is placed in absolute alcohol the dye is removed almost instantaneously from the fibre. In this latter case no chemical operation has been involved, the relations between the dye and the alcohol being simply those of solute and solvent. On the addition of water to the alcoholic solution,

a certain quantity of the colouring matter, the actual amount depending on the degree of dilution of the alcohol, returns to the silk.

Problem of the Unexhausted Dyebath.—A matter of a similar nature to the foregoing is the impossibility often experienced in practice of completely exhausting the dyebath. If, after the material has been dyed as fully as possible in a bath of this type, it is removed from the bath and a second portion introduced, some of the remaining colouring matter will be taken up by the new material, but not the whole of it, and this process can be repeated a number of times without completely exhausting the dyebath.

It is difficult to explain results such as these by means of the chemical theory, for if the process of dyeing simply consists in the formation of a compound between the fibre and the colouring matter, how is it that the introduction of a further quantity of the former does not result in the complete removal of the latter from the dyebath? Of course, behaviour of this kind is not incompatible with the formation of a compound of fibre and dye; it might simply be a case of the establishment of equilibrium in a heterogeneous system made up of the undyed fibre, the dyed fibre, and the dyestuff in solution. But in such a system, where two of the substances are practically insoluble and the third, the dye, soluble, the condition of equilibrium, as arrived at from the application of the Law of Mass Action, is that for each temperature there will be a certain concentration of dye solution with which the dyed fibre can be in equilibrium. If the concentration of

the solution exceeds this equilibrium value, then dye will be taken up by the fibre until the concentration is reduced to the necessary degree, after which no further dyeing will take place; if, on the other hand, a piece of undyed fibre should be placed in a solution of a dye, the concentration of which is lower than the equilibrium value, no dyeing will ensue.

The experiments of Walker and Appleyard [58] showed that these requirements were fulfilled by diphenylamine when dyed with picric acid, but in no known case of ordinary dyeing are the theoretical requirements satisfied, for no matter how dilute a solution of a colouring matter may be, a certain amount of the dye will be taken up from it on the introduction of a fibre. The question of the unexhausted dyebath remains therefore a difficult one to explain by means of the chemical theory.

Experiments with a Liquid as an Artificial Substitute for a Fibre.—Prud'homme [48] thought he might obtain information as to the part played by acid and basic groups of the fibre in fixing dyestuffs by carrying out experiments using an artificial substitute for a fibre in the form of a liquid. He chose a neutral substance which was immiscible with water, such as benzene, chloroform, or amyl alcohol, and in this liquid dissolved an organic acid such as salicylic acid, a weak base, preferably an imide like acetanilide, or a mixture of acid and base; these solutions corresponded to the fibre. Small quantities of the bases of various basic dyes were dissolved in a dilute solution of sodium hydroxide, and two equal quantities of the different solutions

were then measured and mixed, the one with amyl alcohol and the other with the same substance containing 10 per cent. of salicylic acid. The mixtures were rapidly shaken, when it was invariably found that the neutral solution had the natural colour of the base, while the other solution became coloured like the salts of the base.

As silk when dyed with the same colouring matters acquires the same colour as the acid amyl alcohol, it was considered that these results showed that the essential feature in the dyeing of silk with basic colouring matters is the union of the base with the acid group of the fibre. In the same manner it was found that when acidified solutions of acid colouring matters were employed, the colour which resulted when such a solution was shaken with a solution of acetanilide in amyl alcohol was identical with that acquired by wool and silk when treated with the same dye, and it was accordingly considered as proved that the essential feature of the dyeing of animal fibres with acid dyes was salt formation between the acid of the dye and the basic group of the fibre.

Exception was taken by Gillet[30] to the use of salicylic acid and acetanilide in Prud'homme's experiments, on the ground that those substances are appreciably soluble in water, so that the solution in amyl alcohol can scarcely be compared with wool or silk, the acid and basic groups of which are not soluble in water. Gillet employed a 5 per cent. solution of β-naphthol in amyl alcohol in place of the solution of salicylic acid, and obtained results with the aqueous solutions of colour bases which confirmed those arrived at by

Prud'homme. The results with acid dyes, using a solution of β-naphthylamine, were not very conclusive. Gillet doubted whether the acid dyes were fixed by virtue of their acid groups, but thought it more likely that it was through the feebly basic groups often present in acid dyes that union with the fibre took place.

Sisley[53] criticised the results obtained by Prud'homme, Gillet, etc., and stated that amyl alcohol itself becomes coloured when warmed with alkaline solutions of colour bases, the intensity of the colour depending on the alkalinity of the solution. These results obtained by Sisley were attributed by his opponents[29 49] to the presence of small amounts of acid impurities in the amyl alcohol used by him, but he maintained that such was not the case, and that even after thorough purification of the alcohol, the colour was obtained on warming with the solution of the colour base. In view of this observation, no great support for the chemical theory can be found in the results arrived at by Prud'homme and others. Sisley (*loc. cit.*) was of the opinion that these results were better explained by a change in the structure of the colour base, such as had been proved to happen with Magenta, rather than by salt formation with the dissolved acid.

Nature of the Reactive Group in the Fibre.—It will have been noticed that several ideas have been expressed regarding the kind of groups in the fibre with which acid dyes in particular are supposed to combine to form a salt-like product. Experiments conducted by Bentz and Farrell[4] appear to show

that the union is not at any rate with the aromatic primary amino group contained in the fibre. As was mentioned in connection with the fibres, both wool and silk contain a group of this description, which can be diazotised in the usual manner, and the diazo compound then coupled with phenols. If the diazo compound is boiled with water, alcohol, or a solution of cuprous chloride, the nitrogen originally present as the aromatic amino group is removed. Bentz and Farrell showed that wool and silk which had been treated in this manner behaved towards acid dyes in just the same manner as the normal fibres, the dyebaths being equally exhausted and the dyeings equally fast.

Binz and Schroeter[9] suggested that a union between fibre and dye might take place altogether different from the salt formation which most advocates of the chemical theory of dyeing regard as the nature of the action. They pointed out that if the chemical theory in its ordinary form is true, the affinity of dyes for the fibre would be a function of their salt-forming power. This does not agree with many observations, for it has been noticed that the introduction into a chromogen of a sulphonic or carboxyl group does not confer any marked dyeing power on the substance, whereas the introduction of the amino and phenolic groups, whose salt-forming power is much smaller, leads to the production of some of our most powerful dyes. A number of experiments were made with derivatives of azobenzene, and the conclusion was drawn that when amino, sulphonic, and other groups were introduced into the meta

position with regard to the azo group, the substance formed had a certain degree of dyeing power, the mechanism of dyeing appearing to be of the nature of salt formation. When, however, the substituting group entered in the para position to the azo group, the substances formed were powerful dyes, and the process of dyeing appeared to be different in character, since it was not reversible according as acid or alkali was present. Many of the fast wool and silk dyes can be represented as having a quinonoid structure, and Binz and Schroeter considered it probable that they are fixed by a kind of ring condensation between the fibre and the dye, salt formation only coming in as a secondary factor.

The Solution and Adsorption Theories.

It has already been shown that Witt[60] considered the chemical theory in many respects unsatisfactory, and, in 1890, he brought forward another explanation of the dyeing process which he considered to be more in harmony with the observed facts. The new theory, according to which the dye was supposed to exist in the fibre in a state of solution, may be regarded as occupying a position intermediate between the two older theories. In support of his contention, Witt pointed out that in the case of many basic dyes of the triphenylmethane series, such as Methyl Violet and Magenta, the colour acquired by wool or silk when immersed in a solution of the colouring matter is not that of the dry solid but that of the solution; the bronzy green colour characteristic of the solid

dyes is missing from the dyed fabric. If shellac varnish is dissolved in alcohol, and some Magenta is then added, the resultant liquid has a red colour as long as any alcohol remains; when, however, the solvent has all evaporated, the residue has the bronzy colour characteristic of the solid dyestuff. The inference is that the colour is entirely due to the existence of the dye in the state of solution, Magenta being soluble in alcohol but insoluble in shellac. Then, again, Rhodamine, when dissolved in alcohol, gives rise to a fluorescent solution. The solid dyestuff shows no fluorescence, but silk which has been dyed with Rhodamine does exhibit this property, and Witt therefore concluded that the Rhodamine fixed on the silk must be present in a state of solution.

As to why some fibres can be dyed directly with certain colouring matters, while in other cases the agency of a mordant is necessary to effect dyeing, this was explained by Witt by saying that in those cases where a mordant is required the solubility of the dyestuff in the fibre substance is too small to permit of effective dyeing. It is not that the dye is actually insoluble in the fibre, but the solubility is of such small dimensions when compared with the solubility of the colouring matter in water that practically no colouring matter is taken up by the fibre. It will be seen, therefore, that according to the solution theory of the process, the substantive dyeing of a fibre is akin to the extraction of a substance from an aqueous solution by means of an immiscible solvent in which the solubility is greater than in water. An explanation of this kind

certainly provides a reason for the non-exhaustion of the dyebath, which was one of the difficulties of the chemical theory.

Witt only considered the chemical character of the fibre to be of importance in so far as it affected the solvent power of the substance. Silk was considered to be dyed more readily than other fibres because the solubility of dyes in fibroin is greater than in keratin or in cellulose; the solubility of many dyes in cellulose is so small that sodium sulphate or some other salt is added in order to diminish the solubility in the liquor of the dyebath.

As regards adjective dyeing, Witt was of the opinion that the question of solution still had to be considered. In such cases it was, however, the mordant which was dissolved by the fibre, and the solution so obtained then reacted with the colouring matter to form an insoluble compound.

There are certain cases where the dyed material has a colour different from that belonging to the aqueous solution, and Witt anticipated that this might be brought forward as an argument against his theory. He pointed out, however, that phenomena of this kind are by no means unknown in cases of undoubted solution, as for instance with iodine, the aqueous solution of which is brown in colour, while the solution in chloroform has a violet colour. The explanation of these differences of colour is that the iodine exists in the two solutions in different conditions, a feeble union between solvent and solute probably taking place in those liquids from which brown solutions are obtained; the differences ob-

served with dyestuffs might be due to a similar cause.

Objections to Witt's Solution Theory.—It must be admitted that the position taken up by Witt, and the arguments advanced in support of his ideas, strike one at first in quite a favourable manner, but on further consideration certain objections suggest themselves. It was pointed out by von Georgievics [25] that the phenomenon of fluorescence is shown by a number of solid substances, and is not confined to solutions. Moreover, although silk which has been dyed with Fluorescein is fluorescent, yet wool which has been dyed with the same substance shows no fluorescence, and we should therefore, according to the solid solution theory, have to conclude that the Fluorescein is dissolved by the silk and not by the wool, although both fibres are in the dyed state.

The arguments of Witt, based on the colour of Magenta, were also shown to be untenable, for von Georgievics demonstrated that when solid Magenta is rubbed between two glass plates it loses its bronze colour and becomes red. Bronziness, on the other hand, is sometimes observed on dyed goods, as when wool is dyed with a concentrated solution of Magenta. But one of the most apparently destructive pieces of criticism brought by von Georgievics [25 27] against the solid solution theory was that the dyeing process is not reversible. If a dyed fibre is simply a solution, then one would expect that when such a fibre was placed in fresh water it would give up a portion of the colouring matter which it had absorbed, no matter what the nature of the dyestuff might be;

this, however, is by no means the general behaviour of dyed goods, for many dyes are quite fast to washing.

Another anomaly arises from the fact that wool is more readily dyed from a boiling than from a cold solution of a dye, and takes up a larger quantity of colouring matter under the former than under the latter conditions; it might therefore be supposed that the colouring matter is more soluble in the fibre at the higher temperature, and that wool which had been dyed at a high temperature would give up a portion of the colour which it had absorbed when it cooled down again, but this is a mode of behaviour not met with in practice.

Now, if Witt's theory correctly represents the nature of the dyeing process, we should expect the laws governing the distribution of a substance between two immiscible solvents to be obeyed. The work of Nernst and others has shown us that when a substance has the same molecular weight in two solvents the ratio of concentrations of the two solutions after distribution of the substance between the solvents is, at any given temperature, independent both of the quantity of solute and of solvents, and depends only on the solubilities in the individual solvents. If the molecular weight is not the same in the two solvents, this simple ratio is departed from, the ratio of the concentrations of the two solutions varying with the amounts of substances used. Even in such a case it is, however, possible to obtain an expression for the ratio of distribution of the substance between the two solvents. Suppose

the solvents be A and B, and that the molecular weight of a substance when dissolved in the latter solvent be n times as great as when dissolved in the former; then $\frac{C_A}{\sqrt[n]{C_B}}$ will be constant in value, C_A and C_B being the concentrations of the dissolved substance in the two solvents. These are the laws which should be obeyed if the dyeing process is simply one of the formation of a solution in the fibre.

In order to put the question to a practical test, Walker and Appleyard[58] conducted experiments on the dyeing of silk with picric acid. It was found that, for given quantities of silk, water, and picric acid, it was immaterial how the acid was distributed at the beginning of the experiment, the same ultimate equilibrium being arrived at whether the picric acid was only dissolved in the water, all contained in the silk, or partly present in both media at the commencement of the experiment. This result was in harmony with the requirements of the solid solution theory, but would accord equally well with any other theory involving the establishment of a condition of equilibrium. It was also found that the ratio of distribution of the acid between the water and the silk varied with the quantities involved, but that constant values were obtained when a formula was employed of the type already given, the result obtained being

$$\frac{\text{Concentration in silk}}{\sqrt[2.7]{\text{Concentration in water}}} = 35{\cdot}5.$$

A moment's consideration will show that this result is, as far as the dyeing of silk by picric acid is concerned, fatal to the solid solution theory of dyeing as proposed by Witt. If we accept the theory as true, then we are forced to the conclusion that the molecular weight of picric acid in aqueous solution is nearly three times as great as when the acid is contained in silk. Such an idea cannot, of course, be entertained for a moment, for we know that, owing to ionisation, the molecular weight of picric acid in aqueous solution is even less than corresponds with the simple formula $C_6H_2(NO_2)_3OH$, and it is out of the question for the substance to have a smaller molecular weight in a less active solvent such as silk. We must therefore conclude that picric acid does not exist in the silk in a state of simple, homogeneous solution.

Previous to the publication of the paper to which reference has just been made, several other investigations of a similar character had been carried out with varying results. Von Georgievics[26] concluded that when silk is dyed with Indigo-carmine the process is analogous to solution, but his results really lead to conclusions of the same character as those deduced from Walker and Appleyard's experiments; in a later paper, published in conjunction with Löwy,[28] dealing with the distribution of Methylene Blue between water and mercerised cotton, von Georgievics came to the conclusion that his results were incompatible with the solid solution theory. Schmidt[52] could obtain no constant distribution ratio, and considered dyeing to be an absorption phenomenon.

Adsorption Theory.—In actions of this kind where one substance is absorbed by another, but where it is evident that the absorbed substance cannot be in a condition of homogeneous solution, it is considered that the surface of the absorbing substance plays most part in the process of absorption, and the term "adsorption" is made use of to describe such cases of absorption. According to the results of Walker, von Georgievics, etc., we should conclude that in a dyed fibre the colouring matter is not uniformly distributed throughout the fibre, but is collected at the surface; in other words, the process is one of adsorption.* The fact that the surface of a fibre appears to play an important part in the dyeing process may be taken as showing that a certain amount of what may be called mechanical action does really enter into the operation. As has been indicated, however, we cannot explain the whole phenomena of dyeing on a mechanical basis. Many investigations have been carried out during the last fifteen years on this branch of the subject of dyeing, and the results obtained support, for the most part, the view that dyeing cannot be regarded simply as the formation of a homogeneous solution of the dye

* To speak of dyeing as a surface phenomenon may appear to be contrary to the definition of "dyeing" given in the introduction. In this connection it is only necessary to point out that a *fabric* is made up of innumerable individual *fibres*, and that, owing to the fabric being more or less porous, the solution of the dye can penetrate into the material, so that colour can be absorbed by the surface of a fibre in the interior of the fabric; the *material* will not, therefore, be coloured only on its surface.

in the fibre. Amongst those to whom we are indebted for further knowledge on the subject may be mentioned Biltz,[5] Hübner,[32] Freundlich and Losev,[21] Pelet and Grand,[42] Schaposchnikoff,[51] and Brown and M'Crae.[10]

An interesting feature of Hübner's experiments was that attention was particularly directed to the influence exerted on the degree and rate of dyeing by the degree of division of a fibre. In the case of cotton a quantity of yarn was first thoroughly scoured and a portion then disintegrated by treatment in a beating engine. On afterwards introducing equal weights of the beaten and unbeaten fibre into a solution of Night Blue, it was found that while the unbeaten fibre went on steadily absorbing the colouring matter during a period of seventy-two hours, the disintegrated cotton took up the dye very rapidly during the first hour, and very little more was absorbed during the succeeding seventy-one hours. Not only was the rate of absorption greatly accelerated by reducing the state of division of the fibre, but the actual quantity of dye absorbed was also affected, about twice as much colour being taken up by the disintegrated fibre as was absorbed by the unbeaten cotton. These results clearly indicate the part played by the surface of the fibre in the absorption of a colouring matter from aqueous solution, for of course the extent of surface is much greater in the case of the disintegrated fibre than with the unbeaten cotton. On carrying out similar experiments with wool it was found that the rate of absorption was very considerably increased, but there was no increase

in the total amount of dye absorbed. The influence of surface was further shown by experiments with threads of artificial silk of different diameters and with fine- and coarse-grained emery; in both cases the proportion of dye absorbed by the fine sample was greater than that absorbed by the coarser one.

The experiments of many of the later workers on the subject have been partially made with the idea of comparing the absorption of colouring matters by textile fibres with absorption by inorganic substances such as animal charcoal, sand, China clay, aluminium hydroxide, etc. The results clearly show that there is no essential difference between the absorption of dyes by fibres and by inorganic substances, and that in both cases the process is subject to the same laws and appears to be an instance of adsorption. Freundlich and Losev (*loc. cit.*) found that the extent of adsorption is independent of the nature of the adsorbent, a dye which was strongly adsorbed by charcoal also being strongly adsorbed by the textile fibres. Basic dyes were decomposed into acid and base both in the presence of charcoal and of fibres, the acid remaining in solution and the colour base being adsorbed, probably in a polymeric form. In the case of mordant dyeing the adsorption theory can still be applied, the only difference being that it is the mordant which undergoes adsorption.

Although the bulk of the evidence of a quantitative character has been shown to be unfavourable to the simple solid solution theory, there have been several cases put on record of experimental results which

appear to be in harmony with that theory. Brown and M'Crae (*loc. cit.*) showed that when wool is dyed with Acid Magenta in the presence of sulphuric acid and with Chrysoidine FF, the ratio of distribution of the colouring matter between the fibre and the water is practically independent of the concentration of the solution, so that in the case of these dyes it would appear as if the dyeing process is of a nature similar to solution. Sisley[54] also obtained results which he considered to be favourable to Witt's theory.

In concluding this section, reference must be made to another idea regarding solution to which expression was given by Weber.[59] It has already been explained that this chemist regarded the dyeing of fibres with the acid and basic dyes as a process of a chemical nature. He recognised that the absorption of the direct cotton dyes by fibres of different chemical natures could not be explained in the same manner, and he was led to the conclusion that in the case of colouring matters of this class the process was one of solution. Whereas, however, Witt considered the dyestuff to be dissolved by the substance of the fibre itself, Weber was of the opinion that the colouring matter dissolved in the water contained in the pores or intercellular spaces of the fibre. In support of this view he pointed out that cellulose dinitrate can be manufactured in such a manner that it shows little structural difference, when examined by means of the microscope, from ordinary cotton, and these nitrated fibres can be dyed with the benzidine colours in just the same way as ordinary cotton. If the

nitrated cotton is dissolved in acetone, and the solvent allowed to evaporate, a film is left which is devoid of structure and which contains no water. In this form the nitrated cotton cannot be dyed with the benzidine colouring matters. Additional support for this view was obtained by Weber from a microscopical examination of dyed fibres, when in many cases the cell walls appeared colourless, while the lumen was filled with colouring matter.

Other Theories of Dyeing.

An electrical explanation of the attraction of fibres for colouring matters was given by Gee and Harrison.[23] In the case of basic and acid dyes, the colour base of the former and the acid of the latter carry a positive and negative charge respectively derived from the ionisation of the dyestuff. When wool or silk is immersed in water the fibre becomes negatively charged, and it is quite natural therefore that when such a fibre is immersed in a neutral solution of a basic dye there will be an attraction between the negatively charged fibre and the positively charged colour base. When the fibres are placed in an acid solution instead of in pure water they become positively charged; such a change in the kind of electrification with the nature of the solution in which the substance is immersed is frequently noticed with substances of a colloidal character. Under these changed conditions the fibre will now have an affinity for the negatively charged acid of acid colouring matters, while the attraction for basic

dyes will now be less than before in view of the fact that the two are now similarly charged. This latter deduction is quite in keeping with the results obtained in practice, for it is well known that the basic dyes are much less readily absorbed from acid solution than from a neutral one, and this device is sometimes resorted to in order to regulate the rate at which a basic colouring matter is absorbed. This theory also accounts in quite a satisfactory manner for the much smaller attraction shown for dyestuffs of the acid and basic groups by a fibre such as cotton. The potential difference between wool and water is equal on the average to 0·91 volt, while with cotton the average value of the potential difference is only 0·06 volt. Owing to this much smaller charge upon the cotton, it will be readily understood why the fibre should have much less attraction for colouring matters than is shown by wool. While this theory gives an apparently satisfactory explanation of the causes underlying the affinity of fibres for dyestuffs, it does not explain how the colouring matter becomes fixed upon the fibre; for of course after the dye and fibre come into actual contact, it must naturally be assumed that their electrical charges will neutralise each other.

A somewhat similar view was taken by Feilmann,[20] according to whom the coloured ion formed from the dyestuff was attracted by the oppositely charged fibre, and penetrated the latter more or less deeply. The absorbed ion was supposed to be retained, either because the fibre acted as a protective colloid, or because of chemical action taking place between the

ion and the fibre. It will be seen that this idea goes a little further than that of Gee and Harrison, inasmuch as it gives a possible explanation of the means of fixation of the dye on the fibre.

Colloidal Theory.—Of late years a large and ever-increasing amount of attention has been given to the properties and behaviour of colloids. The fibres themselves are of course substances of a colloidal character, and it has been shown in an earlier portion of the book that many dyes when in solution probably exist in the colloidal form. In view of these facts it is not surprising that attempts have been made to explain the dyeing process as a *colloidal* phenomenon. One of the first to take up this view of the matter was Krafft.[39] He pointed out that the substances commonly employed as mordants, such as the hydroxides of iron, aluminium and chromium, tannic acid, soap, etc., are all of a colloidal nature, and suggested that the use of such substances was in many cases necessary in order to combine with dyes of low molecular weight, which under normal conditions only existed in solution to a small degree in the colloidal condition, so as to form a more highly colloidal compound capable of being fixed on the fibre. As for the direct cotton dyestuffs, these were supposed to exist in the colloidal condition to a much greater extent than the dyes of the acid and basic groups, and no assistance was therefore necessary in order to fix the colouring matter. Of course this explanation of the dyeing process, according to which dyeing is simply a precipitation of colloidal substances on or in the fibre, only applies to the dyeing of cotton,

for wool and silk do not require any mordant in order to fix the acid or basic dyestuffs. Pelet-Jolivet and Andersen[43 44] were also in favour of a *colloidal* theory of dyeing.

The view was expressed by several of the supporters of the adsorption theory that the substance actually fixed on the fibre was in the colloidal condition. Freundlich and Losev,[22] for example, considered that in the case of wool dyed with a basic colouring matter, the colour base was adsorbed by the fibre in a colloidal form insoluble in water; and they also considered that in some instances dyeing might be due to the formation of a colloidal compound between the fibre and the dyestuff. Pelet and Grand[42] also considered that dyeing is due to the precipitation of colloids on the fibre, and that the salts added to the dyebath assist in this precipitation. Linder and Picton[41] from experiments made with Methyl Violet, Magenta, Soluble Blue, etc., were led to connect the phenomena of dyeing with the electrical charges which, as is well known, many substances carry when existing in a state of colloidal solution. They found that whereas a colloidal solution of ferric hydroxide is precipitated by the addition of a solution of Soluble Blue, no such action takes place on the addition of Methyl Violet to the ferric hydroxide solution; on the other hand, a colloidal solution of arsenious sulphide is precipitated by solutions of basic dyes like Methyl Violet and Magenta but not by Soluble Blue, an acid colouring matter. The reason is that the charges on the ferric hydroxide and the basic dyes are of a similar nature,

these substances carrying positive charges, while the arsenious sulphide and the Soluble Blue carry negative charges; as is well known, when two oppositely charged colloidal solutions are mixed together they precipitate each other. A difference was noticed, however, between the precipitation of the ferric hydroxide by the acid dye and by means of an electrolyte such as ammonium sulphate. In the latter case a definite amount of the salt is required to completely precipitate the colloid, and any excess which may be added remains in solution. With the dye, however, a different result was observed, for even after the ferric hydroxide had been completely thrown out of colloidal solution it continued to take up the colouring matter as a whole. Linder and Picton explained this on the supposition that a certain portion of the original charge was retained by the ferric hydroxide even after it had been coagulated by the addition of the dyestuff, and that by virtue of this residual charge it continued to take up additional quantities of the dye. The same kind of action was considered to take place during the ordinary process of dyeing, the place of the inorganic colloid being taken by the fibre. They were accordingly of the opinion that the first stage of the dyeing process consisted in the separation of insoluble derivatives of the dye having a feeble charge, these substances being produced as the result of interaction between the dyestuff and the fibre; the second part of the process was an attraction between this coagulum and the remaining dyestuff, the particles of which were retained as a whole.

It will be noticed there is a certain degree of similarity between these views and those expressed later by Gee and Harrison (*loc. cit.*), inasmuch as both pairs of observers consider the electrical condition of the fibre and the dyestuff to play an important part in the process; the differences between the two were that Linder and Picton regarded the matter exclusively from the point of view that the substances with which they were concerned all existed in the colloidal condition, and that they were led to regard the taking up of a dye as proceeding in two stages.

Alexander[1] showed that various protective colloids, such as gelatin and gum arabic, when added to a solution of Benzopurpurin had the effect of causing the mixture to behave in exactly the same manner when treated with acid as wool or silk which had been dyed with the same colouring matter. The addition of a dilute solution of hydrochloric acid to a solution of Benzopurpurin causes the colour to change from red to blue, while on the addition of a more concentrated solution of acid the coagulated dark blue colour acid separates out. If a similar solution of Benzopurpurin is first mixed with one of the above-mentioned colloids the colour is only changed to claret red or chocolate brown on the addition of hydrochloric acid, the colour depending on the concentration of the added acid, and even when concentrated acid is used no precipitate is produced. These changes were investigated by means of the ultramicroscope; it was found that no change resulted in the presence of the colloid, unless the added acid was of sufficient concentration to cause

agglutination of ultramicrons into small groups. As regards the protective action of different colloids, it was found that gelatin was much more effective than gum arabic, and that starch had very little protective action. In the light of these results, it was considered that the difference in colour changes, which result when different fibres dyed with Benzopurpurin are immersed in dilute acid, is due to the difference in protective action of the fibre on the adsorbed colouring matter.

Alexander pointed out that in considering the nature of the combination between the fibre and the dye, it is necessary to bear in mind the state of subdivision of both substances. The usual effect of increase of temperature and of the presence of dilute alkalis is to cause subdivision of the particles of a substance, and it is not surprising therefore that agencies such as these should bring about a closer union between the fibre and the dye, such as Dreaper and Wilson[17 18] had shown to exist. Dreaper and Wilson,[18] in fact, consider that the temperature of the dyebath is the main factor in the actual fixation of the dye on the fibre, and that though in the application of acid dyes the presence of acid in the bath may lead to a larger amount of dye being taken up than would be the case from a neutral solution, yet the acid plays no part in the fixing of the colour. Dreaper and Wilson have shown that it is possible to apply acid dyes from an *alkaline* solution; under such conditions, of course, the substance actually absorbed by the fibre can scarcely be the free colour acid. They consider that the sodium carbonate used

in the bath may act as a salt rather than an alkali, and that it may affect the state of aggregation of the dissolved colouring matter and bring into play conditions more favourable to colloidal action.

Alexander (*loc. cit.*) studied by the aid of the ultramicroscope the effect produced when alkali is added to a solution of Acid Anthracene Red. The appearance of the aqueous solution of this colouring matter would lead one to conclude that a portion of the dye at any rate is in a very fine state of subdivision, if not in true solution. When the dye was dissolved in a solution of sodium carbonate of $N/20$ concentration a certain amount of coagulation took place; but this only represented part of the total quantity of dye actually present, for the alkaline solution, on standing, was found to give only a small amount of sediment, and it also gave a marked Tyndall effect when examined with the ultramicroscope. When a more concentrated solution of sodium carbonate was employed, the bulk of the dye was precipitated; but this precipitate dissolved on being heated, and appeared again when the liquid was allowed to cool. One would infer from this experiment that the state of a dye in solution is modified both by alkali and by change of temperature, and Alexander considered that these factors might explain the fixation of the dye which would, in accordance with the ordinary conditions of dyeing, be absorbed at a high temperature and might be precipitated again on cooling, or be flocculated by adsorbed alkali.

The Divided Nature of the Dyeing Process.

It may have been noticed that in most of the ideas to which expression has been given in the preceding pages, the dyeing process has been regarded as *simple* in character, and the supporters of the different theories have, for the most part, attempted to explain all the phenomena of dyeing as resulting from a single operation. This it is which has led to the various difficulties which have confronted the supporters of the different theories, and which have led some chemists such as Weber [59] and Brown and M'Crae [10] to the conclusion that no one theory can possibly explain all cases of dyeing, and that it may be necessary to adopt one theory to explain the dyeing of one fibre, and another theory to explain the dyeing of a second fibre. This would certainly appear to be the inevitable conclusion if we are to regard the dyeing process as simple in character, that is, as involving one operation only. All the theories have a certain amount of experimental evidence which can be cited in support of them; but they are more or less antagonistic in character, and no one of them will explain the whole of the phenomena associated with the subject of dyeing.

It is the aim of the author in the present section to show that all these opposing theories may be true as *partial* explanations of certain cases of dyeing, and that they may be linked together in one general theory of the dyeing process. In order to arrive that such a result it is necessary to assume at the

operation of dyeing takes place in two distinct stages. Dreaper,[16] Cross and Bevan,[14] Lewis,[40] Zacharias,[61] and Fahrion[19] have all expressed themselves in favour of regarding the dyeing process as having a dual character, and in the opinion of the author it is the most rational view to take of the matter.

In the first part of the process, which may be called *the absorption stage*, the dyestuff is simply absorbed from solution. This absorption was regarded by Zacharias as being brought about by the diffusion of the dissolved dye from the aqueous solution into the fibre, and no particular attraction between the fibre and the dye needs to be invoked to explain this diffusion, although the process may be assisted by electrical attraction. It is the process which takes place naturally when a layer of water is placed over a solution of a dissolved salt, or when a liquid, immiscible with water, is placed in contact with an aqueous solution of a substance which is also soluble in the second solvent. Just as in those cases diffusion is a slow process so that homogeneous solutions are only obtained after the lapse of a considerable time, so also the process of diffusion into the fibre will take place slowly, and although the dye may be said to be dissolved by the fibre, yet, generally speaking, the solute will not be uniformly distributed throughout the fibre but, because of this slow diffusion, will be present in largest quantity at the surface; in other words, the process will appear as an adsorption phenomenon.

The fibres are hygroscopic colloids, and absorb other substances in accordance with certain general

laws. All colloidal substances absorb others according to the law embodied in the expression

$$C_1 C_2^{v} = k,$$

where C_1 and C_2 represent the concentration in the aqueous and in the other phase respectively at the end of the absorption, k is a constant and v a constant coefficient, which may have a value either greater or less than or equal to unity.

It was pointed out by Zacharias that this formula may be deduced mathematically from the laws of diffusion, and accordingly the dyeing of textile fibres and also of other substances such as charcoal, aluminium hydroxide, etc., and the quantitative results obtained in these processes can all be explained on this basis of diffusion of the dissolved dye. The formula is identical with that representing the distribution of a substance between immiscible solvents where homogeneous solutions are formed, but it has already been shown what difficulties are met with if we regard the matter from this latter standpoint.

So far we have only considered the first stage of dyeing; the second part of the process is the *fixation* of the colouring matter. There could be no permanent dyeing without this second operation. Here we have to recognise the fact that dyes may be fixed on fibres as the result of the operation of different forces.

In some cases it seems probable that a certain amount of chemical change takes place, either between the fibre and the dyestuff or in the structure of the

latter compound. Bayliss[2] has put on record a case of dyeing, where a process of absorption was undoubtedly succeeded by one of chemical action. When a dilute colloidal solution of the blue colour acid of Congo Red is mixed with well-washed aluminium hydroxide, the latter absorbs the colour acid and acquires a blue colour; this is adsorption. On suspending the blue precipitate in water and warming the mixture, the colour changes to red owing to the formation of an aluminium salt, chemical action taking place between the colour acid and the basic hydroxide.

No doubt similar chemical changes take place in the dyeing of textile fibres. Cross and Bevan[13] have, in fact, described a very good example of a fibre being dyed as the result of a double process. If jute is immersed in a solution of ferric ferrocyanide it very soon becomes dyed blue owing to the production of Prussian Blue. In this case the substance absorbed is the soluble ferric salt; this then reacts with the jute substance, the unsaturated lignone groups of which are oxidised, and as a result of this action insoluble ferrous ferricyanide is produced and fixed in the fibre.

In other cases the dye may have been originally present in the dyebath in a condition of colloidal solution, and the fixation of the colouring matter may be due to the precipitation of the colloid. Possibly, also, a certain amount of colour may be fixed as the result of adhesion between the fibre and dyestuff.

This theory of the dual nature of the dyeing

process applies to cases of mordant dyeing, to the developed dyes, and those, such as Indigo, which are applied by the vat method, equally well as to all cases of substantive dyeing. In all cases we have a first process of absorption; in the case of the mordant dyes it is usually the mordant which is taken up in this manner, and the mordant is then fixed in an insoluble form. The colouring matter is then absorbed from its solution and reacts with the previously fixed mordant to form the colour lake. The dyeing of cotton with lead chromate and with the azo dyes like paranitraniline red formed directly on the fibre also takes place in two stages, while in the case of the vat dyes we have first the absorption of the soluble leuco compound, and second the fixation of the dye in the insoluble form owing to the oxidation of the leuco compound.

As for the fact that with some colouring matters the dyebath is practically completely exhausted, while with others this is never the case, the probable explanation is that the degree to which the bath is exhausted depends both upon the rate of absorption and on the rate of fixation of the dye. With a dye which is fixed readily and which diffuses into the fibre with considerable velocity, there appears no reason why the dyebath should not be practically exhausted in the period usually occupied by the dyeing process.

This method of regarding the dyeing process also provides an answer to the objections levelled against the solid solution theory with respect to the non-reversible character of the dyeing process. Were

dyeing nothing but an absorption, an extraction of an aqueous solution by means of the immiscible solvent, the fibre, there would be no reason why the process should not be reversible. When, however, the dye becomes fixed, we change its properties either by forming an insoluble compound or by converting it into a modification insoluble in water, and so reversibility of the process ceases to be possible.

In concluding this study of the dyeing process, the author would point out that some at least of the diversity of opinion expressed in the past has been due to the fact that a certain amount of confusion prevailed as to what really constituted the dyeing process. Some workers appeared only to regard the method of fixation of the dye on the fibre; others paid more attention to the process of absorption. As has been shown, the dyeing process embraces both absorption and fixation, and every example of dyeing can be shown to include these two operations. This may therefore be called a general theory or explanation of the nature of the dyeing process. It is true that different methods of fixation of the dyes are recognised, and some may regard this as an objection to a general theory, and as not much of an advance, if any, over the position that no one theory of dyeing can be applied to all cases, but that in some instances the phenomena are to be explained on one basis, and in other cases on a different one. This difference in the mode of fixation is, however, a matter of minor importance due to the great differences in properties of the fibres and dyestuffs; to have reached the stage of being able to say that no matter what the fibre,

no matter what the dyestuff may be, the process of dyeing the one with the other can always be divided into the two stages of absorption and fixation is certainly to have made a very considerable advance in our knowledge of the dyeing process.

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"The Chemistry and Physics of Dyeing," Dreaper.
"Die Theorie des Färbeprozesses," - L. Pelet-Jolivet.

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